

PCT

WORLD INTELLECTUAL PROPERTY ORGANIZATION
International Bureau



1/6

INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

(51) International Patent Classification ⁶ : C03B 37/014	A1	(11) International Publication Number: WO 99/03790 (43) International Publication Date: 28 January 1999 (28.01.99)
(21) International Application Number: PCT/US98/13374 (22) International Filing Date: 24 June 1998 (24.06.98) (30) Priority Data: 60/052,613 15 July 1997 (15.07.97) US (71) Applicant: CORNING INCORPORATED [US/US]; 1 Riverfront Plaza, Corning, NY 14831 (US). (72) Inventors: ANTOS, Alfred, J.; 144 Vanderhoff Road, Elmira, NY 14903 (US). GIROUX, Cynthia, B.; 55211 Chelon Avenue, Wilmington, NC 28409 (US). HOAGLIN, Christine, L.; 4748 Clawson Drive, Campbell, NY 14821 (US). HUNT, Timothy, L.; 5753 Oak Bluff Lane, Wilmington, NC 28403 (US). POWERS, Dale, R.; 112 Weston Lane, Painted Post, NY 14870 (US). WHEDON, William, A.; 1805 Azalea Drive, Wilmington, NC 28403 (US). (74) Agents: HERZFELD, Alexander, R. et al.; Corning Incorporated, Patent Dept., SP FR 02-12, Corning, NY 14831 (US).		(81) Designated States: AL, AM, AT, AU, AZ, BA, BB, BG, BR, BY, CA, CH, CN, CU, CZ, DE, DK, EE, ES, FI, GB, GE, GH, HU, ID, IL, IS, JP, KE, KG, KP, KR, KZ, LC, LK, LR, LS, LT, LU, LV, MD, MG, MK, MN, MW, MX, NO, NZ, PL, PT, RO, RU, SD, SE, SG, SI, SK, SL, TJ, TM, TR, TT, UA, UG, UZ, VN, YU, ZW, European patent (AT, BE, CH, CY, DE, DK, ES, FI, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE). Published <i>With international search report.</i>
(54) Title: DECREASED H2 SENSITIVITY IN OPTICAL FIBER (57) Abstract Disclosed is a method of making a hydrogen resistant optical waveguide fiber. The soot preform is heated and immersed in a metal halide gas. A reduced metal species is thus incorporated into the glass soot prior to sintering or consolidation of the soot preform. A hydrogen absorption band around 1530 nm is substantially eliminated from waveguides made from a precursor gas treated preform.		

BEST AVAILABLE COPY

FP01-0215-02W0-SE
02.2.26
SEARCH REPORT

FOR THE PURPOSES OF INFORMATION ONLY

Codes used to identify States party to the PCT on the front pages of pamphlets publishing international applications under the PCT.

AL	Albania	ES	Spain	LS	Lesotho	SI	Slovenia
AM	Armenia	FI	Finland	LT	Lithuania	SK	Slovakia
AT	Austria	FR	France	LU	Luxembourg	SN	Senegal
AU	Australia	GA	Gabon	LV	Latvia	SZ	Swaziland
AZ	Azerbaijan	GB	United Kingdom	MC	Monaco	TD	Chad
BA	Bosnia and Herzegovina	GE	Georgia	MD	Republic of Moldova	TG	Togo
BB	Barbados	GH	Ghana	MG	Madagascar	TJ	Tajikistan
BE	Belgium	GN	Guinea	MK	The former Yugoslav Republic of Macedonia	TM	Turkmenistan
BF	Burkina Faso	GR	Greece			TR	Turkey
BG	Bulgaria	HU	Hungary	ML	Mali	TT	Trinidad and Tobago
BJ	Benin	IE	Ireland	MN	Mongolia	UA	Ukraine
BR	Brazil	IL	Israel	MR	Mauritania	UG	Uganda
BY	Belarus	IS	Iceland	MW	Malawi	US	United States of America
CA	Canada	IT	Italy	MX	Mexico	UZ	Uzbekistan
CF	Central African Republic	JP	Japan	NE	Niger	VN	Viet Nam
CG	Congo	KE	Kenya	NL	Netherlands	YU	Yugoslavia
CH	Switzerland	KG	Kyrgyzstan	NO	Norway	ZW	Zimbabwe
CI	Côte d'Ivoire	KP	Democratic People's Republic of Korea	NZ	New Zealand		
CM	Cameroon			PL	Poland		
CN	China	KR	Republic of Korea	PT	Portugal		
CU	Cuba	KZ	Kazakstan	RO	Romania		
CZ	Czech Republic	LC	Saint Lucia	RU	Russian Federation		
DE	Germany	LI	Liechtenstein	SD	Sudan		
DK	Denmark	LK	Sri Lanka	SE	Sweden		
EE	Estonia	LR	Liberia	SG	Singapore		

DECREASED H₂ SENSITIVITY IN OPTICAL FIBER

Field of the Invention

The invention relates to a method for decreasing the sensitivity of optical waveguide fiber to hydrogen. In particular, the method markedly reduces hydrogen induced attenuation in single mode optical waveguide fiber in a wavelength band centered about 1530 nm.

Background of the Invention

Hydrogen can react with defects in silica based optical waveguide fibers to form unwanted signal absorption bands. A number of strategies have been developed to avoid the incorporation of hydrogen into the waveguide fiber, including sealed cables, hermetically coated waveguide fiber, and optical fiber cabling materials or coatings which act as hydrogen getters.

An example of the hydrogen getter approach is found in U. S. patent 5,596,668, DiGiovanni et al. ('668). The species for gettering or bonding with hydrogen, in this case a metal, is placed in the clad layer of the waveguide fiber. Diffusion of hydrogen into the light carrying portion of the waveguide is reduced and the waveguide is said to be hydrogen resistant. Care must be taken to prevent inclusion of the getter species into the core region and the part of the clad layer adjacent the core region. These regions carry the signal light and the presence of getter material in the regions would cause unacceptable signal attenuation. The '668 patent at column 3, ll. 65-67 and in Fig.'s 2, 3,

and 4 makes clear the getter material must be located away from the light carrying part of the waveguide. This limitation together with the fact that hydrogen diffusion is not completely eliminated makes this approach less than optimum.

5 Providing the waveguide with a hermetic coating does essentially eliminate hydrogen induced attenuation. However, the application of the coating involves an additional process step which adds considerable cost in terms of raw materials, equipment, and manufacturing rate. Extra measurement steps to insure the hermeticity of the coating are also required.

10 An alternative getter method is one in which the getter material is incorporated in the waveguide polymer coating or in the materials which make up the cable. Such alternatives involve additional expense and the materials must be such that they will not degrade or otherwise leave the host material for the life of the waveguide, which is usually estimated in decades.

15 U.S. patent 4,125, 388, Powers ('388 patent), discloses and claims a method for making high purity optical waveguides, especially waveguides having very low concentrations of water. The inclusion of water in the silica-based glass matrix gives rise to broad absorption bands in wavelength ranges otherwise well suited to signal transmission. The '388 patent discloses and
20 claims a method for making very low water waveguides by removing water from the soot preform during the step in which a soot preform is heated to fuse the soot particles into a glass. The '388 patent discloses the use of Cl_2 gas as a drying agent. The Cl_2 may be fed directly to the preform or a metal halide gas, such as GeCl_4 and SiCl_4 , may be used together with an oxidizing agent to
25 produce Cl_2 in the vicinity of the preform. The drying is carried out within a temperature range in which the soot will fuse into a dense glass.

 In contrast to this drying method, the method of the present invention includes a step which precedes the drying step and which is carried out at a temperature below that at which the preform will be consolidated.

30 Thus there is a need in the waveguide fiber industry for a method of eliminating hydrogen sensitivity which method:

- fits readily into the flow of the existing waveguide fiber manufacturing process;

- does not cause a marked reduction in manufacturing rate;
- is simple and cost effective; and,
- is built into the glass itself and so is reliable over the life of the waveguide.

5

Summary of the Invention

The novel method and the resulting waveguide fiber derived therefrom disclosed and described here, meet the need for a low cost hydrogen resistant waveguide which has excellent long term reliability and which overcomes the deficiencies in the art noted above.

10

One embodiment of the invention relates to a method of making a hydrogen resistant optical waveguide fiber. A soot preform is fabricated by any one of several methods known in the art such as outside vapor deposition or axial vapor deposition. The method can be extended to include a modified

15

inside vapor deposition preform manufacturing method by lengthening the time between soot deposition and soot consolidation or by including an excess of GeCl_4 or SiCl_4 with regard to oxygen. By any of several methods known in the art, at least a part of the central core region of the soot preform is made to have a refractive index higher than at least a part of the surrounding cladding glass layer. These methods can include co-deposition of a soot in the central region to raise the refractive index, co-deposition of a soot in the surrounding layer to lower the index, or treatment of the soot of either region with index modifying gases such as fluorine. Thus, modification of the refractive index can be accomplished during soot deposition or after soot deposition but prior to soot consolidation.

20

25

In one preferred embodiment, the method of deposition is the outside vapor deposition process, and GeCl_4 or SiCl_4 are employed to deposit a GeO_2 doped SiO_2 core region onto a bait rod. This is preferably followed by deposition of at least a minimal amount of a SiO_2 cladding region (additional cladding may also be deposited now or at a later stage, if desired). The bait rod is then removed, and the resultant soot preform can be treated in accordance with the invention. In one such embodiment, a metal halide gas (e.g. GeCl_4) is flowed around the soot preform (and through the hole left by

30

removal of the bait rod, if one was employed to make the preform). Note that in the novel method described herein, the metal halide gas is preferably in excess relative to oxygen. This is in contrast to the smaller metal halide to oxygen ratio which is advantageous in a drying process.

5 In one embodiment of the present novel method, the soot preform is heated to a temperature greater than about 800°C but less than the soot consolidation or sintering temperature. A metal halide gas which is a precursor of a glass forming metal oxide is then caused to flow through or about the hot, porous soot, preferably at a flow rate which is not less than about 0.2 standard
10 cubic centimeters per minute (sccm) per 100 grams of soot glass. As is known in the art, the succeeding process steps can include sintering the soot to form a clear glass body, adding additional overladding if needed or desired, and collapsing or sintering it, and then drawing a waveguide fiber from the resulting draw preform. A flow rate of about 1 sccm or more per 100 g of soot glass is
15 preferred, although a flow rate as low as 0.2 sccm/100g is effective to improve hydrogen resistance. There is essentially no process reason for placing an upper limit on the flow rate. Thus the upper limit is dictated by material cost and equipment capability. A rate of 1.0sccm/100g is well within the capability of the equipment used to dry and sinter the soot preform.

20 The action of the metal halide gas on the soot preform is typically substantially complete in 1 hour. Variability in soot density may require that soot preform be exposed to the metal halide gas for longer time periods or shorter time periods may be effective. A range of about 0.5 to 10 hours has been found to cover the normally encountered range of soot densities and
25 temperatures. In a preferred embodiment of the method, the soot preform is held near in the range of about 1000°C to 1150°C during immersion in the metal halide gas flow. However, the method is effective at least to temperatures as high as 1250°C.

30 The method works well when the index increasing core dopant is germania, although the method will be effective for other core glass dopants. Typical metal halide gases which may be used in the method include GeCl_4 and SiCl_4 .

In an alternative embodiment, the same effect can be achieved by utilizing a soot deposition process, employing a metal halide precursor (GeCl_4) during soot deposition, and employing less than a stoichiometric amount of oxygen in the reaction chamber. In this manner, incorporation of an adequate amount of reduced Ge can be supplied outside the GeO_2 doped core.

A second aspect of the invention is a hydrogen resistant optical waveguide fiber made using the novel method.

A third aspect of the invention is a soot preform and a method of making a soot preform which is a precursor of a hydrogen resistant waveguide fiber.

The method for making the soot preform includes the steps of depositing soot on any of several suitable soot collecting targets known in the art such as a bait rod of carbon, silica, or alumina, or on the inside or outside of a silica based glass tube. The soot comprises a silica layer and a core region of silica doped with an index raising material such as germania. Before sintering, the soot preform is heated and treated with a metal halide gas as before.

A fourth aspect of the invention is an optical waveguide fiber which contains reduced metal species (e.g. reduced germanium) in the core region or in the clad region immediately adjacent the core. The clad region immediately adjacent the core region is a ring of thickness 5 to 10 μm surrounding the core region.

The presence of such reduced metal species is the result of the treatment of the soot preform with a metal halide gas. The reduced metal species may be detected and quantified by any of a number of methods in the art. For example, the presence of reduced Ge may be quantified by measuring the absorption by the waveguide or waveguide glass preform of light having a wavelength near 240 nm. Absorbance is equal to $(1/t)\log(I_0/I)$, where t = sample thickness, I_0 = incident intensity, and I = transmitted intensity. In the case of a glass made from a germanium halide gas treated soot preform, it has been found that an absorbance of not less than about 0.3/mm of 240 nm light, at a radial point located outside the GeO_2 doped region of the core, is indicative of hydrogen resistant glass. In one preferred embodiment, this region is present at or about halfway through the thickness of the adjacent clad ring, or

greater than 1, more preferably greater than 3 microns outside the GeO_2 doped SiO_2 region. More preferably, the absorbance at this wavelength is less than about 0.2/mm. That is, sufficient reduced Ge is present in the glass to make a waveguide fiber which is hydrogen resistant.

5

Brief Description of the Drawings

Fig. 1 is an illustration of a soot preform suspended in a furnace through which a metal halide gas may be flowed.

Fig. 2a is a cross section of a soot preform.

10 Fig. 2b is a cross section of a waveguide fiber or a draw preform.

Fig. 3 is a chart of weight percent GeO_2 versus radial position in a glass preform.

Description of the Preferred Embodiments

15 The novel method of making a hydrogen resistant optical waveguide fiber may be practiced using the soot deposition equipment, preform drying and consolidation equipment, and preform drawing equipment which is used in any of several alternative manufacturing processes known in the art. Fig. 1 shows a soot preform 6, made by any of several alternative processes, suspended by
20 mechanical means 2 in a furnace 4.

Inlet 8 and outlet 10 provide a means of flowing a gas over the soot preform prior to sintering. It is believed that the flow of metal halide gas in this part of the waveguide manufacturing process (consolidation) is most effective in introducing reduced metal species into the soot preform. Further, it is
25 believed preferable that the time lapse between metal halide gas flow and soot sintering be held to a minimum, and can, for example, include flowing the metal halide gas right up until the time that consolidation occurs or is complete . These beliefs are explanatory in nature and are not meant to limit the invention in any way. It will be understood that any of several alternative strategies may
30 be used for flowing the metal halide gas into the furnace. For example, the inlet could be 10 and the outlet 8 in Fig. 1. In some instances the metal halide

gas may be introduced into one or more tubular formations extending horizontally or vertically through the soot preform.

5 Handle 44 is suspended from a support tube 46 for insertion into consolidation furnace 15. Handle 44 comprises glass tube 45 having a flared joint 48 at its upper end and an annular enlargement 49 spaced from the joint 48. Support tube 46 has a slotted handle formed in the end thereof. One side of end region 47 of tube 46 is removed to accept the upper end of handle 44, enlargement 49 resting on slotted base 50 as the adjacent section of tube 45 is inserted into slot 51. At the end of gas conducting tube 53 is a ball joint 52
10 which fits into cavity 54 of joint 48.

The soot preform is preferably exposed to the metal halide gas for a time and temperature which is sufficient to result in a fiber which exhibits decreased sensitivity to hydrogen, e.g. a fiber which exhibits less than .05 dB/km
increased attenuation at 1530 nm after exposure to a 1% hydrogen atmosphere
15 for 6 days, more preferably less than .03 dB/km increased attenuation at 1530 nm after exposure to a 1% hydrogen atmosphere for 6 days, most preferably less than .01 dB/km increased attenuation at 1530 nm after exposure to a 1% hydrogen atmosphere for 6 days. The fact that such fibers, which have a decreased sensitivity to hydrogen, are possible without having to
20 apply a hermetic coating to the fiber is a tremendous advantage over previous fibers. The cross section of a soot preform, Fig. 2a, shows the core soot 11 and the adjacent clad soot layer 12. This porous body made up of core and clad soot is heated in a furnace and immersed in the metal halide gas flow. Once the treatment with the metal halide gas is completed, the soot preform
25 may be sintered to form a glass body and an additional layer of cladding glass 14 may be applied. Typically the extra clad layer is sleeved over or deposited upon the sintered preform. The resulting draw preform is illustrated in Fig. 2b which shows the core region 10, the adjacent clad layer 12 and the outer clad layer 14.

30 The effect of flowing a metal halide gas over the heated soot preform during consolidation is illustrated in Fig. 3. Fig. 3 illustrates weight percent germania versus radial position in a sintered preform for both a metal halide

gas (in this case GeCl_4) treated preform, curve 16, and an untreated preform, curve 18. The excess weight percent GeO_2 present in curve 16 is indicative of additional Ge in the glass matrix. The x-axis is divided into arbitrary units of length. The portion of the preform illustrated in Fig. 3 is only the portion that is located at the interface between the core glass region and the clad glass layer. The excursion of curve 16 above curve 18 indicates that germanium from the GeCl_4 gas flow has been taken up into the preform matrix. The 240 nm light absorbance measurement confirms that the Ge is in its reduced form.

While not wanting to be bound by theory, applicants believe that the mechanism which makes the resulting waveguide fiber hydrogen resistant is as follows. Defects exist in the glass matrix which are due to the presence of excess oxygen. Treating the soot preform with a metal halide (MCl_x , where M stands for metal and x depends upon the metal valence) causes metal atoms to be inserted into the matrix, eliminating surplus oxygen and the associated defect. Thus, treating the soot preform with a pre-selected gas substantially eliminates bonds prone to forming draw induced or otherwise stress induced defects. This model fits well with the behavior of atoms in a glass matrix and does explain pertinent hydrogen absorption bands observed in testing. It will be understood however that the invention is in no way limited by this model and does not depend upon the correctness of the model.

The invention is further illustrated by the following examples which are meant to be illustrative and in no way limiting.

Example 1 (comparative) - Heating without a Precursor Gas

A soot preform was fabricated using an outside vapor deposition method in which glass soot was deposited upon a bait rod. The core region comprising silica and germania was deposited. A layer of silica was deposited about the core region. The bait rod was removed and the soot preform was placed in a furnace and heated to 1000°C . For a 1 hour time period, 20 slpm of He was flowed around the preform and 0.7 slpm of He was passed through the preform center opening. Then for a 3 hour time period, a flow of 0.07 slpm of Cl_2 was added to the flow of He gas in the preform center opening. The Cl_2

flow was stopped and the furnace temperature was raised and the preform was sintered to form a clear glass body. The sintering process is known in the art and will not be further described here. The nominal diameter of the sintered glass body was 7 mm. The portion of the sintered glass body characterized as the waveguide cane had a nominal diameter of 3.5 mm.

The absorption of 240 nm light at three positions in the silica layer was measured to estimate the amount of reduced Ge incorporated therein. The measurements were:

near the core region clad layer interface - 0.27;
0.75 mm further out in the clad from the core - clad interface - 0.09; and,
1.25 mm further out in the clad from the core interface - 0.03. These readings indicate the diffusion of Ge from the core region is not appreciable a few millimeters from the core region.

A waveguide fiber made using this preform was tested in a 1% hydrogen atmosphere for 6 days. The pressure in the testing chamber was 1 atmosphere and the chamber was held at room temperature. The increase in attenuation at 1530 nm was measured to be 1.450 dB/km.

Example 2 - Heating with a Metal Halide Gas

A soot preform was fabricated using a process identical to that in the example above, except that the preform was treated with metal halide gas in accordance with the invention.

The soot preform was placed in a furnace and heated to 1000°C. For a 1 hour time period, 20 slpm of He was flowed around the preform and 0.7 slpm of He was passed through the preform center opening. Then for a 3 hour time period, the center flow was maintained and a flow of 1 sccm/100g of GeCl_4 was added to the 20 slpm flow. The GeCl_4 was stopped and the furnace temperature was raised and the preform sintered to form a clear glass body using a process identical to that in the example above and resulting in an essentially identical sintered preform geometry.

The absorption of 240 nm light at the same three positions in the silica layer as before, was measured to estimate the amount of reduced Ge incorporated therein. The measurements were:

near the core region interface - 2.1;

5 0.75 mm further out from the core interface - 1.8; and,

1.25 mm further out from the core interface - 1.2. This indicates that additional Ge has been incorporated into the metal halide gas treated preform.

A waveguide fiber made using this preform was tested in a 1% hydrogen atmosphere for 6 days. The pressure in the testing chamber was 1
10 atmosphere and the chamber was held at room temperature. The increase in attenuation at 1530 nm was measured to be 0.004 dB/km which is very near the noise floor of the measurement. The incorporation of reduced Ge into the preform in the clad layer adjacent the core region was shown to be effective to
essentially eliminate hydrogen sensitivity in a wavelength band centered at
15 1530 nm.

Although specific embodiments of the invention have herein been disclosed and described, it is understood that such detail is solely for that purpose and variations can be made without departing from the spirit and scope of the invention which is defined by the following claims.

What is claimed is:

1. A hydrogen resistant optical waveguide fiber comprising:
5 a central core region surrounded by and in contact with a clad region,
both of said core region and said clad region comprising a silica based glass;
whereby, said fiber exhibits less than .05 dB/km increased attenuation at
1530 nm after exposure to a 1% hydrogen atmosphere for 6 days.
- 10 2. The fiber of claim 1, wherein said fiber exhibits less than .03 dB/km
increased attenuation at 1530 nm after exposure to a 1% hydrogen atmosphere
for 6 days.
- 15 3. The fiber of claim 1, wherein said fiber exhibits less than .01 dB/km
increased attenuation at 1530 nm after exposure to a 1% hydrogen atmosphere
for 6 days.
- 20 4. A method of making a treated soot preform which is a precursor of a
hydrogen resistant waveguide fiber, comprising the steps of:
fabricating an optical fiber preform comprising a central core region
surrounded by and in contact with a clad region; and, during or after said
fabricating step,
25 exposing said preform to a metal halide gas in an atmosphere and for a
time and temperature which is sufficient to treat said preform so that, when said
preform is employed in a fiber draw process for making an optical fiber, the
resultant fiber exhibits less than .05 dB/km increased attenuation at 1530 nm
after exposure to a 1% hydrogen atmosphere for 6 days.
- 30 5. The method of claim 4, wherein the central core region and the clad region
of said preform in said exposing step are both comprised of silica based soot.

6. The method of claim 5, wherein , more preferably less than than .03 dB/km increased attenuation at 1530 nm after exposure to a 1% hydrogen atmosphere for 6 days.
- 5 7. The method of claim 5, wherein said step of exposing comprises heating the soot preform to a temperature greater than 800°C but less than the sintering temperature of both the core region soot and the clad region soot.
- 10 8. The method of claim 5, wherein said exposing step comprises maintaining the soot preform at a substantially constant temperature.
9. The method of claim 5, wherein said exposing step comprises flowing said metal halide gas around or through said soot preform.
-
- 15 10. The method of claim 5, further comprising sintering the preform to form a clear glass body.
- 20 11. The method of claim 10, further comprising providing additional cladding soot material over the silica layer of the clear glass body to form a draw preform and drawing an optical waveguide fiber from said draw preform.
- 25 12. The method of claim 5, wherein the total metal halide gas flow around or through the soot preform in said exposing step is not less than about 0.2 sccm/100 grams of glass.
- 30 13. The method of claim 12, wherein the gas flow is not less than 1.0 sccm/100 grams of glass.
14. The method of claim 5, wherein the time duration of said exposing step is in the range of about 0.5 to 10 hours.

15. The method of claim 5, wherein the temperature in said exposing step is less than about 1250°C.
- 5 16. The method of claim 5, wherein the temperature in said exposing step is in the range of about 1000°C to 1150°C.
17. The method of claim 5, wherein said core region comprises a region which is comprised of germania soot which is co-deposited with silica soot.
- 10 18. The method of claim 17, wherein said metal halide gas in said exposing step is selected from the group consisting of GeCl_4 and SiCl_4 .
-
- 15 ~~19. The method of claim 5, wherein said metal halide gas in said exposing step is selected from the group consisting of GeCl_4 and SiCl_4 .~~
20. A hydrogen resistant optical waveguide made using the method of claim 4.
21. The method of claim 4, wherein said exposing step occurs during said fabricating step, and said method further comprises depositing SiO_2 soot, along
20 with said metal halide, in an atmosphere having less than a stoichiometric amount of oxygen.
22. The method of claim 21, wherein said metal halide is GeCl_4 .
- 25 23. The method of claim 22, wherein said SiO_2 soot is deposited via chemical vapor deposition using SiCl_4 .
24. A hydrogen resistant optical waveguide fiber comprising:
a core glass region surrounded by and in contact with a clad glass layer,
30 the respective core and clad glass having a refractive index profile and at least a portion of the core glass region having a refractive index which is higher than the refractive index of at least a portion of the clad glass layer;

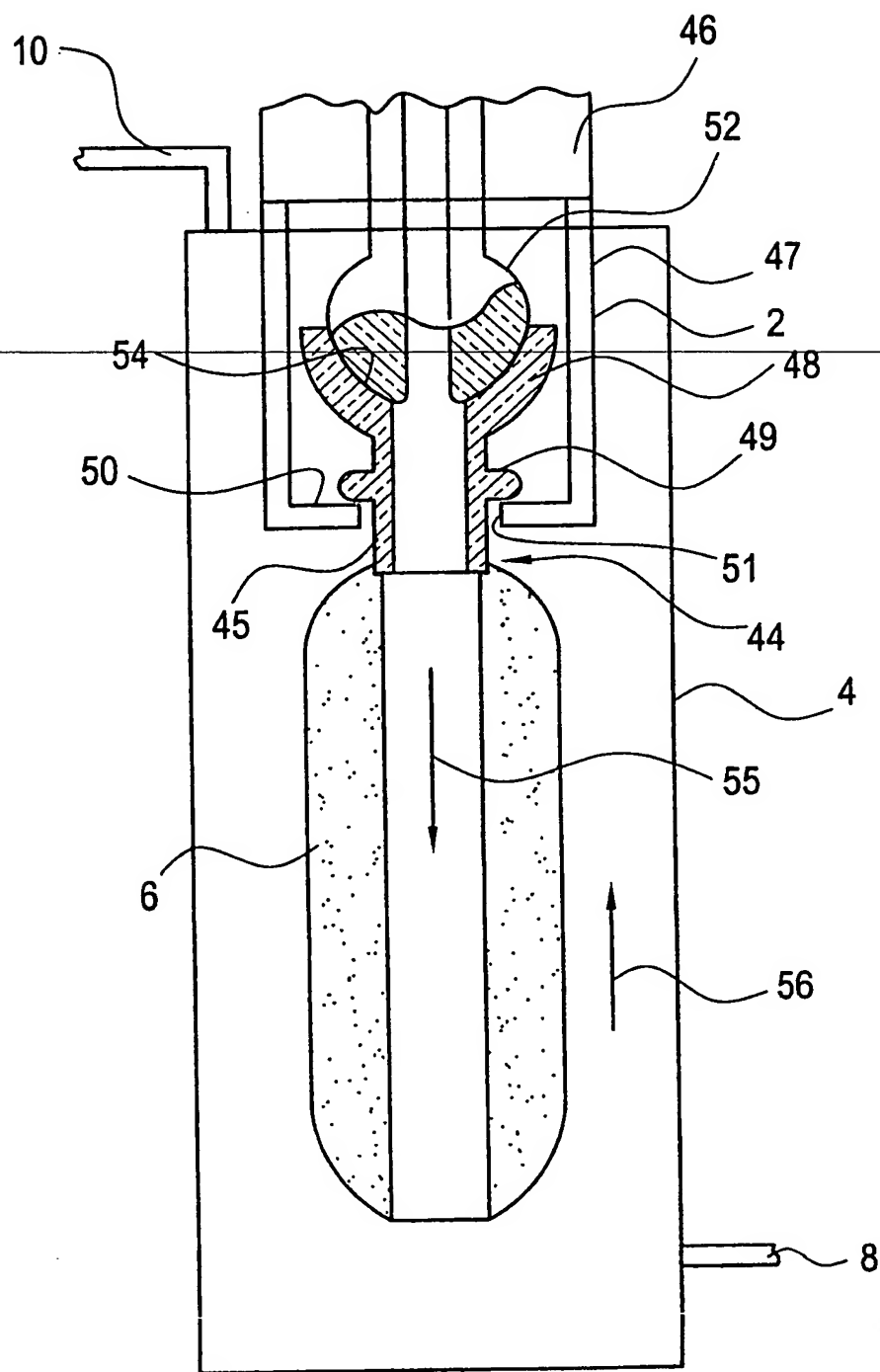
in which at least a portion of the core glass region or a portion of the clad glass region adjacent the core glass region contains a reduced metal species.

5 25. The hydrogen resistant waveguide of claim 24 in which the reduced metal species is selected from the group consisting of Ge and Si.

10 26. The hydrogen resistant waveguide fiber of claim 24 in which the reduced metal species is Ge and the absorbence of 240 nm light directed along the waveguide axis is not less than about 0.2/mm when the radial position of the light is such that the light is absorbed by the clad layer adjacent the waveguide core and no more than 5 to 10 μm from the periphery of the core.

1 / 3

FIG. 1



2 / 3

FIG. 2A

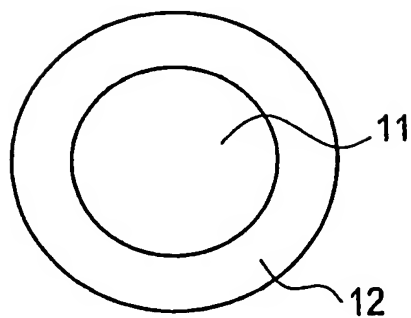


FIG. 2B

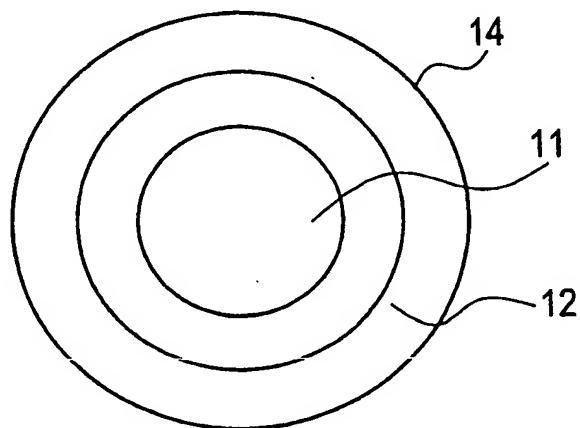
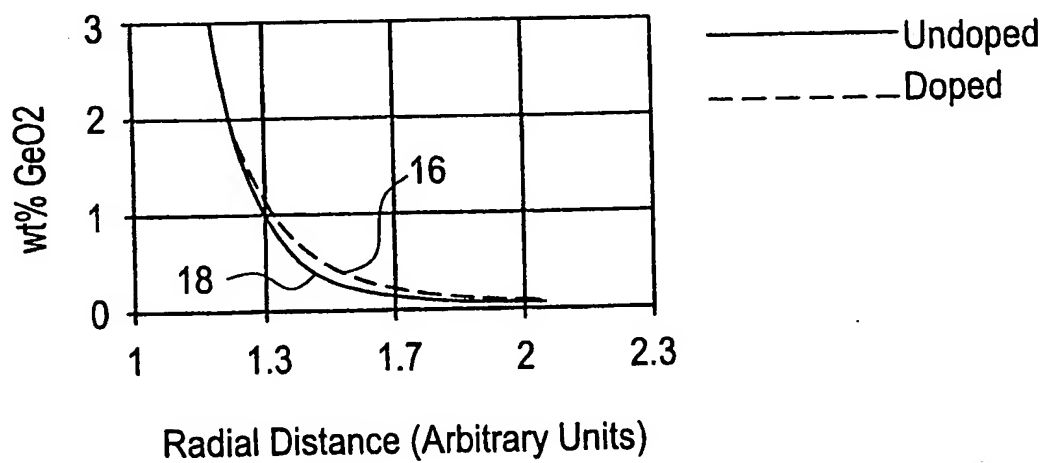


FIG. 3



INTERNATIONAL SEARCH REPORT

International Application No

PCT/US 98/13374

A. CLASSIFICATION OF SUBJECT MATTER
IPC 6 C03B37/014

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

IPC 6 C03B

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	US 5 053 068 A (MICHIHISA KYOTO) 1 October 1991 see the whole document ---	4,7,9
X	US 5 158 587 A (MICHIHISA KYOTO) 27 October 1992 see the whole document ---	4,7,9
X	EP 0 195 407 A (SUMITOMO ELECTRIC INDUSTRIES LTD.) 24 September 1986 see the whole document ---	4,7,9
A	US 4 125 388 A (POWERS) 14 November 1978 see the whole document -----	1-26

☐ Further documents are listed in the continuation of box C.

☒ Patent family members are listed in annex.

* Special categories of cited documents :

- "A" document defining the general state of the art which is not considered to be of particular relevance
- "E" earlier document but published on or after the international filing date
- "L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)
- "O" document referring to an oral disclosure, use, exhibition or other means
- "P" document published prior to the international filing date but later than the priority date claimed

"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention

"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone

"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.

"&" document member of the same patent family

Date of the actual completion of the international search

6 October 1998

Date of mailing of the international search report

13/10/1998

Name and mailing address of the ISA
European Patent Office, P.B. 5818 Patentlaan 2
NL - 2280 HV Rijswijk
Tel. (+31-70) 340-2040, Tx. 31 651 epo nl,
Fax: (+31-70) 340-3016

Authorized officer

Van den Bossche, W

INTERNATIONAL SEARCH REPORT

Information on patent family members

International Application No

PCT/US 98/13374

Patent document cited in search report		Publication date	Patent family member(s)	Publication date
US 5053068	A	01-10-1991	JP 1794016 C	14-10-1993
			JP 5001223 B	07-01-1993
			JP 61247633 A	04-11-1986
			US 5158587 A	27-10-1992
<hr/>				
US 5158587	A	27-10-1992	JP 1794016 C	14-10-1993
			JP 5001223 B	07-01-1993
			JP 61247633 A	04-11-1986
			US 5053068 A	01-10-1991
<hr/>				
EP 195407	A	24-09-1986	JP 1794005 C	14-10-1993
			JP 5001222 B	07-01-1993
			JP 61215224 A	25-09-1986
			JP 1909461 C	09-03-1995
			JP 6039335 B	25-05-1994
			JP 62083331 A	16-04-1987
			AU 579454 B	24-11-1988
			AU 5474386 A	25-09-1986
			CA 1290942 A	22-10-1991
			CN 1020190 B	31-03-1993
			US 5364428 A	15-11-1994
			US 5145507 A	08-09-1992
			US 5203899 A	20-04-1993
<hr/>				
US 4125388	A	14-11-1978	AT 377964 A	28-05-1985
			DE 2806931 A	23-08-1979
			FR 2418775 A	28-09-1979
			GB 1597041 A	03-09-1981
			NL 7802167 A,B,	29-08-1979
			AT 125578 A	15-10-1984
<hr/>				